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GAS PHASE CATALYTIC FLUORINATION OF HALOGENATED HYDROCARBONS
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4

1. Process for gas phase catalytic fluorination of a halogenated hydrocarbon by means of hydrofluoric acid, in which process there is used a mixed catalyst based on chromium and vanadium derivatives, these two elements being predominantly in the oxidation state III.

2. Process according to Claim 1, in which the chromium and the vanadium are in the oxidation state III to the extent of more than 90 %.

3. Process according to Claim 1 or 2, in which the V/Cr atomic ratio is between 0.1 and 3.5.

6. Process according to Claim 5, in which the bulk catalyst is obtained by calcining at between 200 and 600°C a precipitate or gel of compounds of chromium(III) and of vanadium(III) or by thermal decomposition of chromium(III) and vanadium(III) oxalates.

8. Process according to any one of Claims 1 to 4, in which the chromium and vanadium compounds are deposited on a support.

12. Process according to any one of Claims 1 to 11, in which 1-chloro-2,2,2-trifluoroethane is fluorinated to 1,1,1,2-tetrafluoroethane.

The present invention relates to the manufacture of fluorinated hydrocarbons by gas phase catalytic fluorination of halogenated hydrocarbons by means of hydrofluoric acid and its subject is more particularly the use of catalysts based on chromium and vanadium.

Intensive research conducted into the substitutes for chlorofluorocarbons (CFCs) is directed, inter alia, towards the synthesis of fluorinated hydrohaloalkanes. Some stages of this synthesis can be carried out by heterogeneous gas phase catalytic fluorination by means of hydrofluoric acid.

Since these hydrohaloalkanes are frequently compounds that are more complex than the CFCs and, above all, chemically more reactive than the latter, their synthesis requires the development of more active and more selective catalysts.

~~Very many metal compounds (for example~~
chromium, cobalt, nickel, manganese, magnesium, vanadium, copper etc) exhibit a catalytic effect on these fluorination reactions. The catalysts proposed in the literature are either in bulk or supported, the supports commonly employed being chiefly carbon, alumina (partially converted into AlF_3 after fluorination) or aluminium trifluoride.

The combination of chromium and vanadium is

known for the preparation of oxidation catalysts. Thus, European Patent EP 002,682 claims a bulk catalyst based on vanadium and chromium oxides for the oxidation of aliphatic hydrocarbons to carboxylic acids.

5 In the field of fluorination, few documents mention the use of vanadium in fluorination catalysts.

In this context, European Patent EP 295,885 describes the synthesis of F134a (1,1,1,2-tetrafluoroethane) by gas phase fluorination of a
10 halogenated olefin on a catalyst based on hexavalent chromium and on a transition metal which are supported on alumina. The transition metal more particularly preferred is titanium. Vanadium is mentioned but not exemplified. Starting with solid alumina, the
15 impregnation is ensured by aqueous solutions of chromium(VI) oxide and of salts of transition metals; at the end of preparation the chromium is still in the VI state and the other metal is in an oxidized form (oxidation state IV in the case of titanium).

20 Furthermore, European Patent EP 203,807 describes the preparation of fluorinated olefins by transhalogenation, employing a catalyst based on chromium oxide or aluminium oxide combined with a compound of other elements, including vanadium. The
25 mixed ones based on vanadium are not exemplified and the basic reaction is not a fluorination reaction within the meaning of the present invention.

Vanadium is also employed for liquid phase

fluorination. European Patent EP 503,792 describes the fluorination of haloalkanes with a transition metal fluoride such as vanadium pentafluoride.

Similarly, Bardin et al. [J. Fluor. Chem. (1990) 49(3) 385-400] describe the liquid phase fluorination of olefins (addition of two fluorine atoms). The fluorinating agent employed is VF₃, synthesized by direct fluorination of vanadium metal using fluorine.

10 It has now been found that in gas phase fluorination of saturated or olefinic halogenated hydrocarbons, using HF, the use of mixed Cr-V catalysts in which the vanadium and the chromium are predominantly in the oxidation state III makes it possible to obtain catalytic performance superior to
15 that obtained with chromium by itself or with vanadium by itself. Furthermore, the use of vanadium and of chromium in the III state makes it possible to reduce considerably the losses of vanadium while avoiding the
20 formation of volatile vanadium(V) oxyfluorides or fluorides. The mixed Cr-V phases in the oxidation state III therefore enable the catalytic performance to be improved while limiting the losses of active species.

 The present invention therefore provides a
25 process for gas phase catalytic fluorination of halogenated hydrocarbons by means of hydrofluoric acid, in which process there is used a mixed catalyst based on chromium and vanadium, these two elements being

predominantly in the oxidation state III.

"Predominantly" is intended to mean that at least 80 % (preferably more than 90 %) of the elements chromium and vanadium are in the oxidation state III.

5 In the catalyst according to the invention, which may be bulk or supported, the V/Cr atomic ratio may range from 0.05 to 5. It is advantageously between 0.1 and 3.5, preferably between 0.15 and 3.

The catalyst to be employed in accordance
10 with the present invention can be prepared from chromium and vanadium precursors, using processes that are known per se for obtaining bulk or supported catalysts.

Chromium precursors that may be mentioned are
15 chromium oxides, hydroxides, halides, oxyhalides, nitrates, acetates, oxalates and sulphates, but it is also possible to employ any other chromium compound which allows a homogeneous mixture of chromium and vanadium in solid phase to be produced. For the
20 preparation of bulk catalysts the preferred precursors are chromium salts such as the chlorides and more particularly the sulphates, acetates and nitrates. For the preparation of supported catalysts it is preferred to employ chromium(III) chloride or chromic anhydride
25 (CrO_3).

Available vanadium precursors are few in number. Chlorides, acetylacetonates, oxychlorides and oxysulphates may be mentioned, vanadium(III) chloride

being more particularly preferred.

By way of example without any limitation being implied, a method of preparation of bulk catalysts according to the invention consists in the neutralization of the abovementioned chromium(III) and vanadium compounds with a base (sodium hydroxide, aqueous ammonia, amines etc) or else in the reduction of CrO_3 in the presence of an abovementioned vanadium compound. The precipitate or the gel obtained is then washed and then dried before being calcined at a temperature of between 200 and 600°C.

A bulk catalyst according to the invention can also be obtained by thermal decomposition (200 to 450°C) of chromium and vanadium oxalates precipitated in an organic medium (alcohols, ethers, chlorinated hydrocarbons etc).

The final catalyst can be formed by any suitable technique known to a person skilled in the art (tableting, extrusion, granulation etc). Various additives may be added to the preparation to enhance the physicochemical and catalytic properties of the final product. It is thus possible to add (% on a mass basis relative to the mass of the final catalyst) for example:

- 2 to 30 % of powdered Cr_2O_3 or $\text{Cr}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$ dried beforehand at 300°C, or $\text{Al}_2\text{O}_3 \cdot x\text{H}_2\text{O}$ in order to improve the mechanical behaviour of the final catalyst,
- 0.1 to 5 % of graphite and/or 0.1 to 10 %

of polyvinyl alcohol to facilitate the forming by
tableting or extrusion,

- 0.1 to 20 % of flocculant such as
polyacrylates or polyacrylamides to facilitate the
5 filtration of the cake recovered after neutralization.

In the case of the supported catalysts the
support employed must be compatible with the media
containing HF. Supports commonly employed such as
aluminium trifluoride and metal oxides such as alumina,
10 magnesia and zirconia are suitable. In the case of
these oxides, which are generally fluorinated under an
HF atmosphere (exothermic reaction producing water), it
is often preferable to subject them to fluorinating
conditions before their impregnation with the chromium
15 and vanadium compounds. This impregnation of the
support may be carried out, for example, by means of an
aqueous solution of CrCl_3 and of VCl_3 , or by means of two
aqueous solutions, one containing CrO_3 , the other
containing VCl_3 and a reducing agent such as methanol.

-
- 20 In some cases the support (carbon) may also be involved
as a reducing agent. In such a supported catalyst the
total chromium and vanadium content may range from 0.5
to 25 % by weight, preferably between 2 and 15 %.

The mixed Cr-V catalysts according to the
25 invention can be employed for the gas phase
fluorination of saturated or olefinic halogenated
hydrocarbons using HF. They are particularly suitable
for the fluorination of halogenated hydrocarbons

resulting in C₁-C₄ fluorinated compounds containing one or more hydrogen atoms. The following compounds may be mentioned as examples of starting halogenated hydrocarbons, without any limitation being implied:

- 5 CHCl₃, CH₂Cl₂, CCl₂=CHCl, CHCl₂-CClF₂, CHCl₂-CF₃, CHFCl-CF₃, CH₃-CCl₃, CH₃-CFCl₂, CH₃-CF₂Cl, CH₂Cl-CF₃, CH₃-CCl₂-CH₃, CCl₃-CF₂-CH₃, CCl₃-CF₂-CHCl₂, CCl₃-CF₂-CH₂Cl, CHCl₂-CHCl-CH₃, CH₂Cl-CHCl-CH₃, and CCl₂=CCl₂; this last compound does not contain hydrogen, but the addition of
- 10 HF results in hydrohalogenated compounds.

For working at optimum activity the catalyst requires a treatment with hydrofluoric acid, undiluted or diluted with nitrogen. Although the presence of vanadium slows down the crystallization, such an

15 activation can locally generate temperatures higher than 500°C. This is why it is recommended to control the exothermicity of the activation by relying on the addition of a diluent for HF and by beginning this treatment at low temperature (150-250°C). On the other

20 hand, after the "exothermicity waves" in the catalyst bed have passed, it is recommended to raise the temperature gradually to reach a maximum of 350-450°C at the end of activation.

When the unactivated catalyst contains a high

25 concentration of chromium and/or vanadium in an oxidation state higher than three, it is appropriate to undertake a reduction stage (heat treatment between 200 and 400°C in a neutral or reducing atmosphere) before

the activation, to prevent the latter from resulting in a considerable loss of vanadium and/or chromium due to formation of volatile species.

The temperature of fluorination of the organic materials depends on the reaction studied and quite obviously on the desired reaction products. Thus, in the case of an addition of HF to a double bond or a partial substitution of chlorine atoms with fluorine, the work is done at temperatures of between 50 and 350°C. Substitution of all the chlorine atoms generally requires temperatures of between 300 and 500°C.

The contact time also depends on the reaction studied and the intended products. In most cases it is between 3 and 100 seconds; however, to obtain a good compromise between the degree of conversion and space time yield, the contact time is advantageously shorter than 30 seconds.

The molar ratio HF/organic compound(s) is also related to the reaction studied. It depends, inter alia, on the stoichiometry of the reaction. In most cases it can vary between 1/1 and 20/1 but, here again, in order to obtain high space time yields, it is often lower than 10.

The working pressure is preferably between 1 and 20 bars absolute (0.1 to 2 MPa).

Depending on their mechanical toughness, the catalysts according to the invention can work in a stationary bed or in a fluid bed. The catalysts whose

activity has dropped as a result of fouling can be regenerated by purging the catalyst with a compound capable of oxidizing and converting the products (organic materials, coke etc) deposited on the catalyst
 5 into volatile products. Oxygen or a mixture containing oxygen (for example air) is perfectly suited for this purpose and enables the initial activity of the catalyst to be restored.

In order to ensure the regeneration of the
 10 catalyst without giving rise to a crystallization of the catalyst or to an oxidation of the vanadium and chromium it is recommended to perform this treatment at
 : a temperature not exceeding 350°C. It is therefore
 : appropriate to limit the exothermicity of this
 :
 15 "combustion" by controlling the flow rate of oxygen (a low flow rate of oxygen diluted in an inert gas at the beginning of regeneration) so as to maintain a
 : temperature lower than 350°C.
 :
 :

To maintain the activity of the catalyst it
 20 ~~is also possible to perform the fluorination reaction~~
 in the presence of oxygen introduced in a molar ratio O_2 /organic compound which may range from 0.001 to 0.05 and is preferably between 0.005 and 0.03. In this case it is recommended to work at a temperature not
 25 exceeding 400°C to avoid an oxidation of the vanadium and of the chromium.

The following examples illustrate the invention without limiting it.

PREPARATION OF THE CATALYSTS

Catalyst 1

20 g (0.05 mol) of chromium nitrate nonahydrate $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and 1.57 g (0.01 mol) of vanadium trichloride VCl_3 , were dissolved in 100 ml of water and the solution was then neutralized to pH 6.4 by means of 14 ml of 14N NH_4OH . The gel obtained was washed with water and then filtered off and dried in the oven for 14 hours at 120°C. The powder thus obtained was then calcined under nitrogen at 350°C for 4 hours.

Catalyst 2

A solution of 32 g of ammonium oxalate monohydrate, 1.15 g of vanadium trichloride and 27 g of chromium nitrate nonahydrate in 75 ml of water was prepared at 50°C with stirring. The clear solution thus obtained was cooled and then poured rapidly into a mixture of 375 ml of ethanol and 375 ml of ethylene glycol.

20 The mixed complex $(\text{NH}_4)_3[\text{Cr}_x\text{V}_{1-x}(\text{C}_2\text{O}_4)_3]$ thus obtained was then decomposed in air at 350°C, producing an amorphous catalyst of chromium and vanadium oxides.

Catalyst 3

Same preparation as catalyst 2, but with a double quantity of VCl_3 (2.3 g) and a smaller quantity of $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (24 g).

Catalyst 4 (comparative)

Same preparation as catalyst 1, but with VCl_3 ,

replaced with 1.73 g (0.01 mol) of vanadium
oxytrichloride VOCl_3 .

Catalyst 5

Same preparation as catalyst 1, but with VCl_3 ,
5 replaced with 1.73 g of VOCl_3 , and with the calcination
performed with a mixture of nitrogen and hydrogen (N_2/H_2 ,
molar ratio: 95/5) to reduce V^{V} to V^{III} .

Catalyst 6 (comparative)

32 g of ammonium oxalate monohydrate and 13 g of VOCl_3 were mixed with stirring in 75 ml of water at 60°C . The oxalic complex thus obtained was then decomposed in air at 350°C , producing a vanadium(V) oxide catalyst.

Catalyst 7

15 In a rotary evaporator are placed 30 ml of a support containing 73 % by weight of aluminium fluoride and 27 % of alumina, obtained in a preceding stage by fluorination of alumina of large surface area ($> 180 \text{ m}^2/\text{g}$) in a fluidized bed at about 300°C with the

20 aid of air and hydrofluoric acid (a concentration of 5 to 10 % by volume of this acid in air).

Two separate aqueous solutions are also prepared:

(a) chromic solution containing:

25 - chromic anhydride (CrO_3) : 3.2 g
 - water : 3 g

(b) methanolic solution containing:

- vanadium trichloride (VCl_3) : 5 g

- methanol	:	3.8 g
- water	:	9 g

The mixture of these two solutions is then introduced onto the support, with stirring, at ambient temperature at atmospheric pressure and over
5 approximately 45 minutes. The catalyst is then dried in a stream of nitrogen, in a fluidized bed at about 110°C for 4 hours.

Catalyst 8 (comparative)

10 Same preparation as catalyst 7, but without reduction of the chromium with methanol, the methanolic solution of VCl_3 being replaced with a solution of 5 g of VCl_3 in 11 ml of water.

Catalyst 9

15 Same preparation as catalyst 7, but with the support being impregnated with a single solution containing 8.5 g of chromium(III) chloride hexahydrate, 5 g of VCl_3 and 14 g of water.

Catalyst 10

20 Same preparation as catalyst 7, but with the methanolic solution of VCl_3 replaced with a solution containing 5.4 g of VOCl_3 , 3.8 g of methanol and 5 g of water.

Catalyst 11 (comparative)

25 Same preparation as catalyst 7, but with the methanolic solution of VCl_3 replaced with a solution of 5.4 g of VOCl_3 in 8 g of water.

Catalyst 12 (comparative)

Same preparation as catalyst 7, but without vanadium, using a chromic solution of 3.2 g of CrO_3 in 5 g of water and a methanolic solution containing 3.8 g of methanol in 7 g of water.

Catalyst 13 (comparative)

Same preparation as catalyst 7, but without chromium, the support being impregnated with a single solution containing 5 g of VCl_3 , 10 g of water and 2 g of methanol.

FLUORINATION OF F133a

The performance of catalysts 1 to 13 and that of an amorphous Cr_2O_3 bulk catalyst (catalyst 14 hereinafter) were tested, after activation, in the fluorination of 1-chloro-2,2,2-trifluoroethane (F133a) at atmospheric pressure.

The hydrofluoric acid employed is a commercial product containing only traces of water and the starting F133a is a 99.9% pure product. The reactor employed is a 20-ml Inconel tube heated by a tubular oven.

The activation of the catalyst with HF is carried out in this reactor on a 15-ml sample. After drying for 2 hours at 200°C under nitrogen (0.1 mole/hour), HF is added gradually at this same temperature. After the exothermicity peaks have passed, the HF flow rate is increased to reach 0.1 mole/hour and the temperature is then raised to 350°C .

A temperature plateau is observed with these conditions for 10 hours.

Before being introduced into the reactor the reactants are mixed and heated to the reaction temperature in an Inconel preheater.

After washing with water (to remove the hydracids) and drying over CaCl_2 , the reaction products are analysed in line by gas phase chromatography.

Table I which follows shows the main characteristics of the activated catalysts and the percentage losses of vanadium during the activation.

The operating conditions for the fluorination of F133a and the results obtained are collated in Tables II and III.

TABLE I

Characteristics of the activated catalysts

Catalyst No.	BET surface area (m ² /g)	ELEMENTAL ANALYSIS (weight %)				Vanadium loss %
		Cr	V	Al	F	
<u>Bulk</u>						
1	43.4	45.9	7.1	0	19.7	7
2	50.5	47.6	2.4	0	35	7
3	52.4	42.2	6	0	31.2	9
4 Comp.	56.4	49.5	6.4	0	19.2	25
5	55.8	48.3	7.6	0	18.5	10
6 Comp.	32	0	48.1	0	24	not measured
14 Comp.	110	54	0	0	21	-
<u>Supported</u>						
7	51.6	4	3.8	26.6	60.6	5
8 Comp.	43	5.2	1.3	26.6	62.3	40
9	45.9	6.1	4.8	25.3	59.2	3
10	54.5	6.6	2.6	24.8	59.6	28
11 Comp.	47	7.1	1.4	26.8	61.9	53
12 Comp.	39.5	6.3	0	27.2	61.8	-
13 Comp.	36.3	5	4.3	27.7	62.6	3

TABLE II
Fluorination of F133a to F134a at 350°C and atmospheric pressure
Bulk catalysts

TEST	F1	F2	F3	F4	F5	F6	F7	F8	F9	F10	F11
<u>Operating conditions:</u>											
Catalyst No.	1	1	1	2	3	4	5	14	14	14	6
HF/F133a molar ratio	4.5	4.1	4	5.2	4.2	4.1	4.2	3.9	4.2	3.8	3
O ₂ /F133a molar ratio	0	0	0.005	0	0	0	0	0	0	0.005	0
Contact time (seconds)	4	2.1	0.5	3.6	4	3.9	3.8	4.2	3.9	0.6	3.5
Catalyst age (hours)	20	46	133	24	24	25	23	67	340	24	23
<u>Results:</u>											
Overall degree of conversion of F133a (%)	21.2	21.3	20.1	22.6	21.1	22.9	21.5	20.9	15.5	15.1	3
Selectivity (mol%) for:											
- F134a (CF ₃ CH ₂ F)	97.1	97.5	93.3	97.4	97.4	95.8	95.9	95.7	97.1	92.3	34.8
- F1122 (CF ₂ =CHCl)	0.9	0.9	1.6	0.9	0.7	1.3	1.4	1	1	1.1	4.6
- F120 series (*)	1.2	0.7	3.3	0.8	0.4	0.7	0.6	1	0.6	4.8	0.3
- F143a (CF ₃ CH ₃)	0.5	0.6	0.2	0.2	0.8	0.9	0.7	1.4	0.3	0.3	59.6
- others	0.3	0.3	1.4	0.7	0.7	1.3	1.4	0.9	1	1.5	0.7

* Combined hydropentahalothanes

TABLE III

Fluorination of F133a to F134a at 350°C and atmospheric pressure
Supported catalysts

TEST	F12	F13	F14	F15	F16	F17	F18	F19	F20	F21
<u>Operating conditions:</u>										
Catalyst No.	7	7	8	9	9	10	12	12	12	13
HF/F133a molar ratio	4.5	4.1	4.1	4	4	4.1	3.8	3.9	4	4
O ₂ /F133a molar ratio	0	0.00 5	0	0	0	0	0	0	0.00 5	0
Contact time (seconds)	4	0.5	4	3.9	4	3.9	4.1	4.2	0.5	4
Catalyst age (hours)	20	24	43	24	250	24	24	151	23	19
<u>Results:</u>										
Overall degree of conversion of F133a (%)	19.3	15.2	21.8	20.5	20.1	20.9	20.7	15.2	12.3	3
Selectivity (mol%) for:										
- F134a (CF ₃ CH ₂ F)	98.4	96.7	98.1	98.2	98.1	97.4	97.9	98	96.6	78.4
- F1122 (CF ₂ =CHCl)	0.7	1	0.9	0.6	0.7	1.2	1.3	0.7	0.9	11.7
- F120 series (*)	0.5	1.4	0.5	0.8	0.9	0.6	0.3	0.3	1.6	9.3
- F143a (CF ₃ CH ₃)	0.4	0.5	0.5	0.4	0.3	0.3	0.4	0.3	0.6	0.3
- others	0	0.4	0	0	0	0.5	0.1	0.7	0.3	0.3

• Combined hydropentahaloethanes

Insofar as the bulk catalysts are concerned, the results obtained in tests F1 to F3 and F7, and more particularly that with a short contact time (test F3), reflect the better activity of the mixed $\text{Cr}^{\text{III}}\text{-V}^{\text{III}}$ catalysts when compared with chromium(III) oxide by itself (tests F8 to F10) or vanadium(V) oxide by itself (test F11). Tests F1 to F5 show that the methods of preparation: the sol-gel route (catalyst 1 - tests F1 to F3) and the oxalate route (catalysts 2 and 3 - tests F4 and F5) result in comparable catalytic performance.

Inspection of Table I shows that the losses of vanadium during the activation of the catalyst are low when precursors of chromium and of vanadium in the oxidation state of three are employed (catalysts 1 to 3). The losses during the activation are greater when a precursor of vanadium in an oxidation state higher than three is employed (catalyst 4), unless a reductive calcination is carried out before the activation (catalyst 5).

In the case of the supported catalysts the results obtained in tests F15 and F16 also show the better stability of the mixed $\text{Cr}^{\text{III}}\text{-V}^{\text{III}}$ catalysts when compared with Cr_2O_3 by itself (tests F18 and F19).

The mixed catalyst ex Cr^{VI} and V^{III} supported on AlF_3 (catalyst 8) exhibits a good activity (test F14), but the losses of vanadium during the activation stage are considerable (40 %). These losses appear to be due to an oxidation-reduction reaction between chromium(VI)

and vanadium(III).

The claims defining the invention are as follows:

1. Process for gas phase catalytic fluorination of a halogenated hydrocarbon by means of hydrofluoric acid, in which process there is used a mixed catalyst based on chromium and vanadium derivatives, these two elements being predominantly in the oxidation state III.
2. Process according to Claim 1, in which the chromium and the vanadium are in the oxidation state III to the extent of more than 90 %.
3. Process according to Claim 1 or 2, in which the V/Cr atomic ratio is between 0.1 and 3.5.
4. Process according to Claim 1 or 2, in which the V/Cr atomic ratio is between 0.15 and 3.
5. Process according to any one of Claims 1 to 4, in which the mixed Cr-V catalyst is a bulk catalyst.
6. Process according to Claim 5, in which the bulk catalyst is obtained by calcining at between 200 and 600°C a precipitate or gel of compounds of chromium(III) and of vanadium(III) or by thermal decomposition of chromium(III) and vanadium(III) oxalates.
7. Process according to Claim 5 or 6, in which the bulk catalyst is prepared from vanadium(III) chloride and a chromium sulphate, acetate or nitrate.
8. Process according to any one of Claims 1 to 4, in which the chromium and vanadium compounds are

deposited on a support.

9. Process according to Claim 8, in which the support is aluminium trifluoride or a metal oxide.

10. Process according to Claim 8, in which the support is alumina, magnesia or zirconia.

11. Process according to any one of Claims 8 to 10, in which the supported catalyst is prepared from vanadium(III) chloride and chromium(III) chloride or chromic anhydride.

12. Process according to any one of Claims 1 to 11, in which 1-chloro-2,2,2-trifluoroethane is fluorinated to 1,1,1,2-tetrafluoroethane.

13. Process according to Claim 1 substantially as described in the Examples.

14. A fluorinated hydrocarbon prepared by the process claimed in any one of Claims 1 to 13.

DATED this SEVENTH day of DECEMBER 1994
Elf Atochem S.A.

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ABSTRACT

GAS PHASE CATALYTIC FLUORINATION OF HALOGENATED HYDROCARBONS

The invention relates to the gas phase catalytic fluorination of halogenated hydrocarbons by means of hydrofluoric acid.

A mixed catalyst based on chromium and vanadium derivatives is employed, these two elements being predominantly in the oxidation state III.

Using this catalyst, improved catalytic performance is obtained.
